

## Novel Monomeric Phenanthroline - Thallium(III) Complexes Multinuclear NMR Characterization in Organic Solvents

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**Abstract:** A novel complex of monomeric thallium(III) with the nitrogen donor ligand phenanthroline (phen) has been prepared and characterized by multinuclear NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>205</sup>Tl). The three complexes exist in equilibria in DMSO and acetonitrile solution, which was proved by the <sup>205</sup>Tl NMR spectra. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of tris-phen Tl(III) complex have been measured, where the spin-spin coupling between Tl (*I* = 1/2) and <sup>13</sup>C or <sup>1</sup>H signals were observed with the <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy in acetonitrile. The coupling constants are presented and the chemical shifts of complexes are discussed in detail.

**Keywords:** Thallium(III), phenanthroline (phen), N-donor ligands, NMR spectroscopy.

Thallium(III) complexes with nitrogen donor ligands constitute an interesting field in coordination chemistry. Phenanthroline is an extremely stiff organic ligand. The stability constants of its coordination compounds with Tl(III) have been investigated in aqueous solution by potentiometer<sup>1</sup>. <sup>205</sup>Tl NMR technique has provided an effective method to study the thallium(III) solution chemistry. Thallium(III) coordination chemistry has attracted considerable attention recently for its rich coordination geometry, even if this metal ion is difficult to study in aqueous and organic solvents due to its strong hydrolytic and oxidative properties<sup>2,3</sup>. Tl(III) is considered as a soft metal ion. Tl(III) complexes with inorganic ligands, like chloride and bromide, have been studied previously<sup>4-6</sup>. With N-donor ligands, like ethylenediamine and 2,2'-bipyridine, Tl(III) forms stable complexes with bidentate ligand coordination<sup>7</sup>. In order to further investigate the rich coordination geometry of Tl(III) in solution, we report here the synthesis and multinuclear NMR characterization of Tl(III)-Phen complexes in solution.

### Results and Discussion

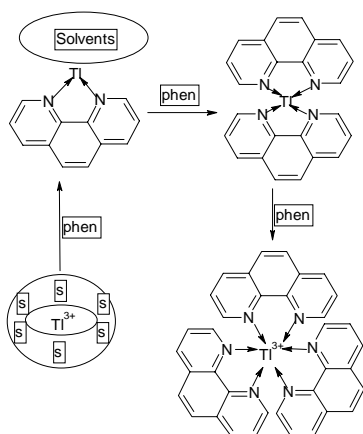
#### *NMR characterization in solution*

<sup>205</sup>Tl NMR of [Tl(phen)<sub>n</sub>]<sup>3+</sup> (n = 1~3) complexes

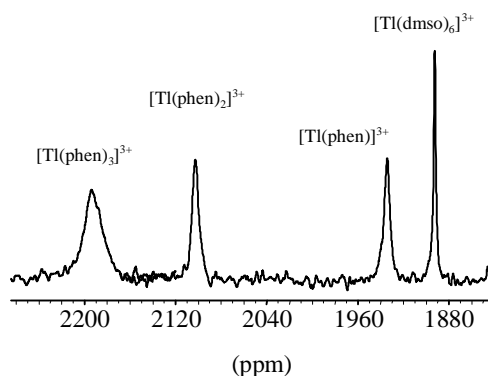
For the <sup>205</sup>Tl NMR spectra of a solution of [Tl(dmsO)<sub>6</sub>]<sup>3+</sup> in DMSO only one signal was observed, which belongs to the species [Tl(dmsO)<sub>6</sub>]<sup>3+</sup> ( $\delta$  = 1890 ppm, 20 mmol/L Tl<sup>3+</sup>).

When phenanthroline ligand was gradually added to this solution, the equilibria would shift to  $[\text{Tl}(\text{phen})_n]^{3+}$  complexes, the  $^{205}\text{Tl}$  NMR signals at 1933 ppm, 2102 ppm and 2192 ppm are assigned with help of NMR titration (**Figure 1**) to the complexes of  $[\text{Tl}(\text{phen})]^{3+}$ ,  $[\text{Tl}(\text{phen})_2]^{3+}$  and  $[\text{Tl}(\text{phen})_3]^{3+}$  respectively, which exist in equilibria in solution (**Scheme 1**). No other phen complexes were formed under the chosen experimental conditions. In a similar way, three complexes of  $[\text{Tl}(\text{phen})_n]^{3+}$  ( $n = 1\sim 3$ ) were characterized in acetonitrile by  $^{205}\text{Tl}$  NMR spectroscopy (**Table 1**). The chemical shifts of three complexes are slightly shift to the low field (or high frequency) relative to those in DMSO, which are probably due to the different solvation in the Tl(III) coordination sphere.

**Scheme 1** Step formation of  $[\text{Tl}(\text{phen})_n]^{3+}$  complexes,  $n = 1 \sim 3$ .



**Figure 1** 288 MHz  $^{205}\text{Tl}$  NMR spectra of the complexes of  $[\text{Tl}(\text{phen})_n]^{3+}$  in DMSO.  $[\text{Tl}(\text{III})]=20$  mmol/L,  $[\text{phen}]=0\sim 80$  mmol/L.

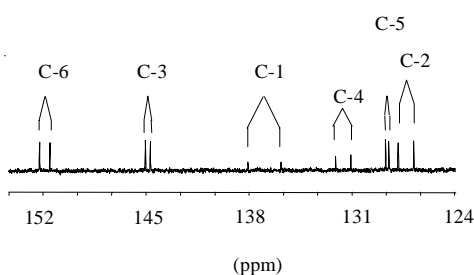


### $^{13}\text{C}$ and $^1\text{H}$ NMR spectra

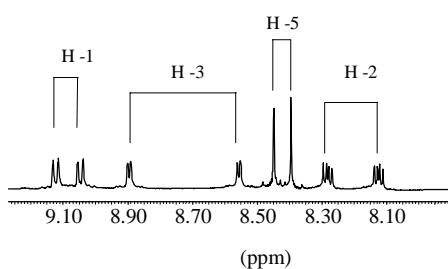
The  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra of tris-phen thallium(III) complex of  $[\text{Tl}(\text{phen})_3]^{3+}$  were measured by dissolving the solid complex of  $[\text{Tl}(\text{phen})_3](\text{ClO}_4)_3$  in DMSO and acetonitrile. On its  $^{205}\text{Tl}$  NMR spectrum, only one signal of complex  $[\text{Tl}(\text{phen})_3]^{3+}$  was detected in two different solvents. The  $^{13}\text{C}$  and  $^1\text{H}$  NMR data of this complex were listed in **Table 1**. Comparing with the spectrum of free ligand, the similar pattern and chemical shifts were obtained in two different solvents. It is very interesting that all the spin-spin coupling of  $^{205}\text{Tl}$  ( $I = 1/2$ ) with all the carbons and protons in the complex were observed in acetonitrile (**Table 1**), but not in DMSO (**Figure 2** and **3**). This is very similar to the Tl-bipy system both in spin-spin coupling constants and chemical shifts as we studied previously<sup>7</sup>. It can be supposed that because of the much stronger donor ability of the DMSO ligands ( $\text{DN} = 29.8$ ), compared to  $\text{CH}_3\text{CN}$  ( $\text{DN} = 14.1$ )<sup>8</sup>, the former has enough capacity to compete with the phen ligand. Because of different coordination ability of the two kinds of solvents, it will cause different exchange kinetic

mechanism, and make the NMR spectrum quite different in two solvents. The broad band of the  $^{205}\text{Tl}$  NMR of tris-phen thallium(III) complex can also show that the exchange process gets fast in DMSO (**Figure 1**).

**Figure 2**  $^{13}\text{C}$  NMR spectrum of the complex  $[\text{Tl}(\text{phen})_3](\text{ClO}_4)_3$  in  $\text{CD}_3\text{CN}$ . 50 mmol/L of  $[\text{Tl}(\text{phen})_3](\text{ClO}_4)_3$  in  $\text{CD}_3\text{CN}$ .

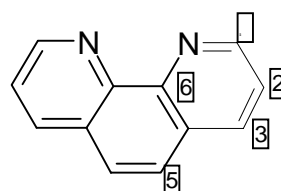


**Figure 3**  $^1\text{H}$  NMR spectrum of the complex  $[\text{Tl}(\text{phen})_3](\text{ClO}_4)_3$  in  $\text{CD}_3\text{CN}$ . 50 mmol/L of  $[\text{Tl}(\text{phen})_3](\text{ClO}_4)_3$  in  $\text{CD}_3\text{CN}$ .



**Table 1** The NMR data of the monomeric thallium complexes in organic solution

Species	$^1\text{H}$ NMR (J Hz) ppm	$^{13}\text{C}$ NMR (J Hz) ppm	$^{205}\text{Tl}$ NMR ppm
$[\text{Tl}(\text{phen})_3]^{3+}$ in DMSO	H-2: 8.14, H-5: 8.43	C-2: 126.53, C-5: 127.82	$[\text{Tl}(\text{dmsO})_6]^{3+}$ 1890
	H-3: 8.88, H-1: 9.07	C-4: 129.74, C-1: 137.01	$[\text{Tl}(\text{phen})_n]^{3+}$ (n=1-3)
		C-3: 142.02, C-6: 149.41	1933, 2102, 2192
$[\text{Tl}(\text{phen})_3]^{3+}$ in $\text{CH}_3\text{CN}$	H-2: 8.19 ( $^3\text{J}$ : 79)	C-2: 128.24 ( $^3\text{J}$ : 128)	$[\text{Tl}(\text{dmsO})_6]^{3+}$ 1882
	H-5: 8.42 ( $^4\text{J}$ : 27)	C-5: 129.47 ( $^4\text{J}$ : 27)	$[\text{Tl}(\text{phen})_n]^{3+}$ (n=1-3)
	H-3: 8.72 ( $^4\text{J}$ : 121)	C-4: 132.28 ( $^3\text{J}$ : 123)	2037, 2137, 2253
	H-1: 9.08 ( $^2\text{J}$ : 39)	C-1: 137.40 ( $^2\text{J}$ : 269)	
	C-3: 144.92 ( $^4\text{J}$ : 39)		
	C-6: 151.60 ( $^2\text{J}$ : 82)		



#### $^{205}\text{Tl}$ chemical shifts

The effect on chemical shifts in NMR is dominated by the nuclear shielding, which includes diamagnetic and paramagnetic term of Ramsey equation<sup>9</sup>. The diamagnetic term is mainly due to the core electrons and can determine the chemical shifts of the lightest nuclei. On the heavier nuclei, this diamagnetic contribution remains constant

and paramagnetic term will determine the chemical shift<sup>10</sup>. A theoretical study of the chemical shifts of metal NMR in metal ion complexes by *ab initio* finite perturbation SCF method showed that for heavy atoms the paramagnetic term is 10-100 times larger than diamagnetic contribution<sup>11</sup>. Closed shell *p* and subshells *d* give no contribution to the paramagnetic term, which is caused by donation of electrons from the ligands to the metal's outer *p* orbitals and by the back donation of electrons from the metal *d* orbitals to the ligands. Highly electronegative ligands withdraw more  $\sigma$  electrons from fully occupied  $d_{\sigma}$  orbitals to the ligands. This  $\sigma$  interaction produces holes in the (n-1)*d* shell of the metal<sup>11</sup>. The coordinated nitrogen (phen) is highly electronegative and attracts electrons from Tl  $d_{\sigma}$  orbitals. The electron cloud density of the thallium atom in its N-bonded complexes is lower than without ligands. The more N-ligands attach to the  $Tl^{3+}$ , the lower electron cloud density around the thallium ion. This effect causes a deshielding of the thallium nucleus; thus, its chemical shifts increases. The phen is similar in property to bipy, the scale of the change on chemical shifts is almost the same. For the more high electronegative ligands of ethylenediamine(en) and diethylenetriamine (dien), the large scale of increasing their chemical shifts has been observed by <sup>205</sup>Tl NMR spectra compared with phen and bipy<sup>7</sup>.

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